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EFFECT OF ORGANIC LIQUIDS ON CRACK
PROPAGATION IN GLASS

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A study was conducted on the effect of straight chain organic alcohols and alkanes having chain lengths between 5 and 16 carbon atoms on crack propagation in various glasses. The test was a modification of the double cantilever beam technique. Tests performed in the alcohols yield plots of crack velocity versus stress intensity factor K which were tri-modal, similar to those for glass tested in N_2 gas of varying relative humidity. Experiments in the alkanes (except for pentane) yielded similarly shaped curves. Crack velocities in the two lowest K regions were independent of alcohol chain length and were controlled by water dissolved in the —continues		

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alcohol, fitting a model derived by Wiederhorn for the effect of water on crack propagation. An effect of the chain length of the alcohol was observed only in the water independent, high- K region, where crack velocity increased monotonically with decreasing chain length at a given K . It was shown that the activation energy for crack growth in this third region, although dependent on the type of analysis used, suggested that alkali ion diffusion in the glass controlled crack growth rates. There was no systematic effect of glass composition within the soda-lime-silica system or in fused silica, but crack velocities at a given K in a $3\text{BaO} \cdot 5\text{SiO}_2$ glass were higher under all conditions than those in soda-lime glasses.

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EFFECT OF ORGANIC LIQUIDS ON CRACK PROPAGATION IN GLASS

INTRODUCTION

The primary objective of this study was to determine the effect of both straight chain alcohols and alkanes on the relationship between crack velocity and stress intensity factor in glass. The incentive for this investigation was in part due to the recent work of Westwood and coworkers [1-3], who found interesting effects of these liquids on a number of glass properties, some of which involved the resistance of the glass to crack propagation. Preliminary results indicated that the effect of dissolved water on crack growth behavior must be taken into account. Even though the longer chain alcohols ($N > 6$) and the alkanes dissolve little water, it will be shown that the crack propagation behavior of glasses in most of these liquids can be explained by extending a model derived by Wiederhorn [4] for the effect of water on crack propagation in glasses to include water dissolved in other liquids. The effect of glass composition and especially sodium ion concentration was investigated, since the theories of Westwood and coworkers [1-3] would suggest that crack propagation should be sensitive to this parameter.

THEORY

The model derived by Wiederhorn [4] to explain the effects of water on crack propagation in glasses is based on the diffusion of water through a stagnant boundary layer at the crack tip at which it reacts with the glass. The reaction rate was assumed to follow the law of Hillig and Charles [5]. Since in the present study we are dealing with liquids rather than gases, a modification of the model was necessary. For instance it is unlikely that long chain alcohols could exist at the crack tip, so that the liquid boundary layer must end some distance from the tip. Since the partial pressure of water in the gas in front of the boundary will be the same as that in the liquid surface, Wiederhorn's model would predict the same form for crack propagation behavior under these conditions.

Wiederhorn was able to show that two distinct regions of behavior could be defined, a low-velocity low-stress-intensity-factor- K regime (region 1) in which crack velocities are governed by the rate of stress corrosion, and a higher K region (region 2) in which the rate of diffusion of water to the crack tip controls velocities.

Wiederhorn's model suggests that the relationship between crack velocity, stress intensity factor, and water content in region 1 should be of the form:

$$V = \frac{Ax_0^n e^{bK}}{n}, \quad (1)$$

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where x_0 is the overall concentration of water in the liquid or gas and can be taken as the partial pressure of water, i.e., relative humidity (RH), n is the order of the chemical reaction, K is the stress intensity factor, and A and b are constants. From Eq. 1 a plot of $\log V$ versus $\log RH$ at constant K would be linear with slope n . Wiederhorn found however that the actual data did not follow a single straight line but that at lower humidity the slope n was approximately 1/2 whereas at higher RH the slope n was 1, suggesting a change in the order of the chemical reaction taking place at the crack tip.

For region 2, Wiederhorn's model results in the following expression for crack velocity:

$$V = \frac{C D_{H_2O} x_0}{\delta n} \quad (2)$$

where D_{H_2O} is the diffusivity of water in the solvent, δ is the boundary layer thickness, and C is a constant. A plot of $\log V$ versus RH for this region should be a straight line of slope equal to 1. Wiederhorn found the data for glass tested in N_2 gas of varying humidity to follow such a curve and that crack velocity was relatively insensitive to K .

Wiederhorn and others have experimentally observed a third region of crack propagation behavior (region 3) in which crack velocities are independent of the presence of water. This region occurs at higher K values and is theorized to be due to a different mechanism.

EXPERIMENTAL PROCEDURE

Glasses used in this study consisted of a commercial soda-lime-silica composition (microscope slides), fused silica, and some experimental glasses. The proportions of major constituents in all glasses are presented in Table 1. Details on the preparation of the $3BaO \cdot 5SiO_2$ glass are given elsewhere [6]. The experimental soda-lime-silica glasses were prepared by mixing appropriate quantities of reagent grade raw materials in 200-gram batches. The glasses were contained in a Pt-20Rh crucible, melted in a SiC-resistor furnace at about 1400°C, stirred for approximately 2 hours with a Pt-20Rh stirrer, allowed to fine for approximately 20 hours, and poured into a graphite mold to form plates. The plates were annealed for 1 hour at 550°C and furnace-cooled to room temperature. Refractive-index measurements indicated no compositional variations within a batch. Specimens were cut from the plates and ground to the appropriate dimensions for use in the crack propagation experiments (12 by 50 by 1 mm). No effect could be noted of reannealing the glasses after specimen preparation.

The test employed for the crack propagation studies was a modification of the double cantilever beam configuration (Fig. 1) in which a constant moment rather than a constant force is applied to the specimen. The stress intensity factor for this test is given [7] by

$$K = \frac{M}{\sqrt{It}} \quad (3)$$

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Table 1
Glass Compositions

Glass	Major* Components (wt - %)			
	SiO ₂	Na ₂ O	CaO	BaO
1 (commercial)	72.0	14.0	7.0	—
2	69.7	20.2	10.1	—
3	65.9	25.0	9.1	—
4	59.0	12.6	28.4	—
5	38.8	—	—	60.5
6 (Corning Code 7940)	99.9	—	—	—

* Minor impurities and additions of Al₂O₃ and MgO in commercial glass were neglected for the purposes of this study.

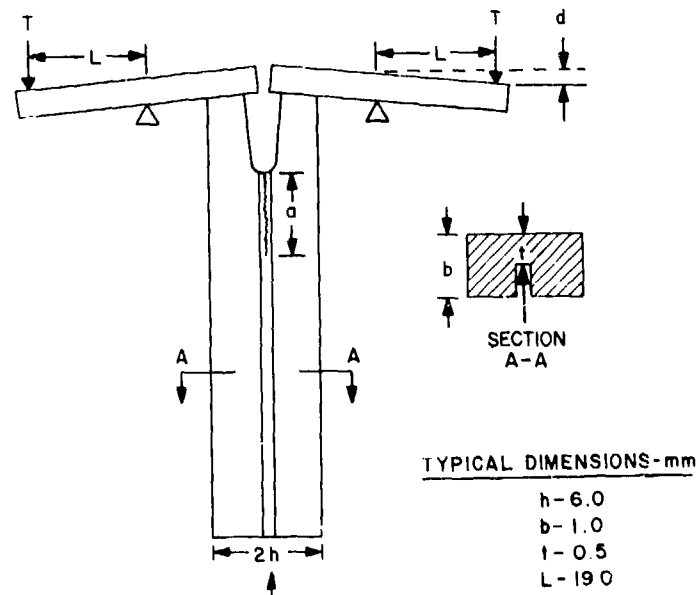


Fig. 1 — Specimen configuration for the double cantilever beam test employing a constant applied moment.

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where M is the bending moment applied to one side of the specimen, I is the moment of inertia of one leg about its longitudinal axis of symmetry, and t the thickness of the specimen at the groove used to guide the crack. The major advantages of this test are the independence of K with respect to crack length and the elimination of the need for corrections for shear and end effects such as arise in the more usual double cantilever arrangement. Further details concerning this test are given elsewhere [7].

The crack was initiated in the glass in air by tightening a pointed screw against the ungrooved side. During testing, the bottom half of the specimen was inserted in a beaker containing the liquid, making sure the crack tip was always submerged. The organic liquids employed were reagent grade alcohols having from six (hexanol) to 12 (dodecanol) carbon atoms and reagent grade alkanes (Fisher Scientific) varying from five (pentane) to 16 (hexadecane) carbon atoms. The water content was measured using a hygrometer (Panametrics, Inc.) having a sensor that could be immersed in the fluid. Alcohols having less than six carbon atoms were not investigated because of their greater affinity for water. The relative humidity (RH) of the alcohol always increased with time of exposure to the atmosphere (Fig. 2). Large values of relative humidity were achieved by allowing the alcohol to form a layer over water in the bottom of the test beaker. Very low values of relative humidity could not be obtained for some of these alcohols because the rate of absorption of water at these levels was large compared to the time of the experiments.

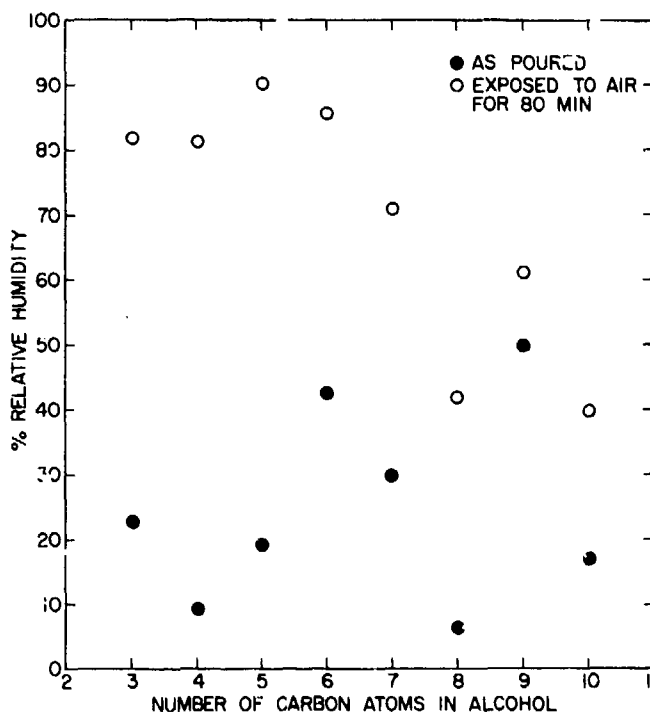


Fig. 2 — Relative humidity of the alcohols as a function of time of exposure to the atmosphere

Exposure to water however, produced only a slight increase in relative humidity in the alkanes, which generally fell in the range of 25 to 50%. Because of the difficulty in changing the water content in the alkanes, no correlation of crack velocity with humidity was attempted.

Tests were performed in the alcohols at temperatures up to 130°C maintained by an immersed resistance heater connected to an on-off controller. The temperature in the liquid at the specimen surface was measured with a mercury thermometer.

RESULTS

Crack velocities plotted as a function of stress intensity factor K are shown in Fig. 3 for specimens tested in water as well as in the alcohols. The graph for octanol was obtained from a least-squares fit for each segment of the curve, requiring that the sum of the residuals for all three segments be minimized. Because of the effect of the water

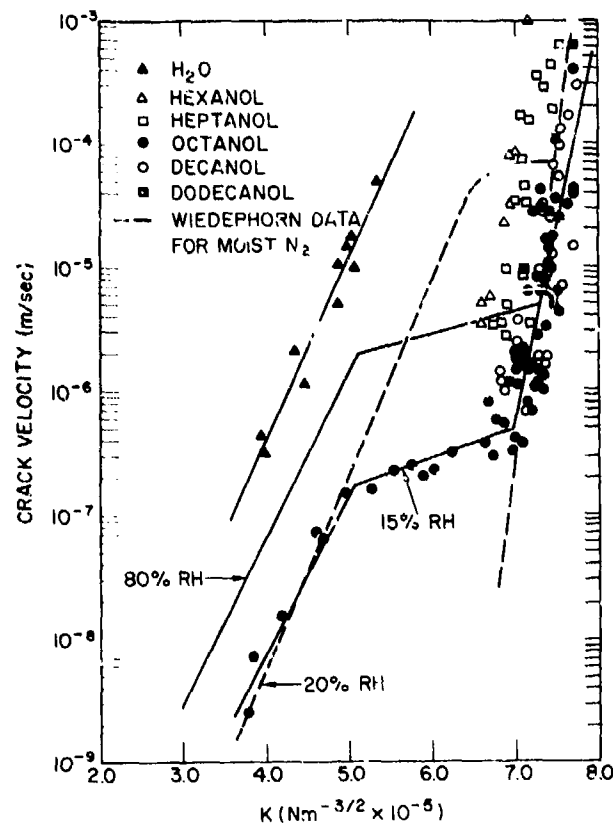


Fig. 3 — Crack velocity as a function of K for commercial soda-lime-silica glass tested in water and various alcohols

content of the alcohols on crack velocities, only region-3 (water-independent) data for the other alcohols is presented here. The data are compared in Fig. 3 with data obtained by Wiederhorn [4] for water in nitrogen gas, and the only major differences occur in region 2. The similarity between the behavior of the glass in region 1 in both the alcohol and N_2 gas reinforces the concept that the stress corrosion rate at the crack tip controls its velocity. In region 2, where Eq. 2 shows that the diffusivity of water as well as the boundary-layer thickness should have an effect on crack velocity, one would expect to see differences due to the solvent. The quantitative differences between the velocities at which diffusion control begins in N_2 gas and alcohols can be ascribed to the differences in diffusion rates of water and the boundary-layer thicknesses in these media; that is, a lower diffusivity of water in alcohol than in N_2 would lead to smaller crack velocities.

Fig. 4 presents a logarithmic plot of crack velocity versus relative humidity, as suggested by Wiederhorn's model, for a constant stress-intensity factor in each of the three regions in Fig. 3.

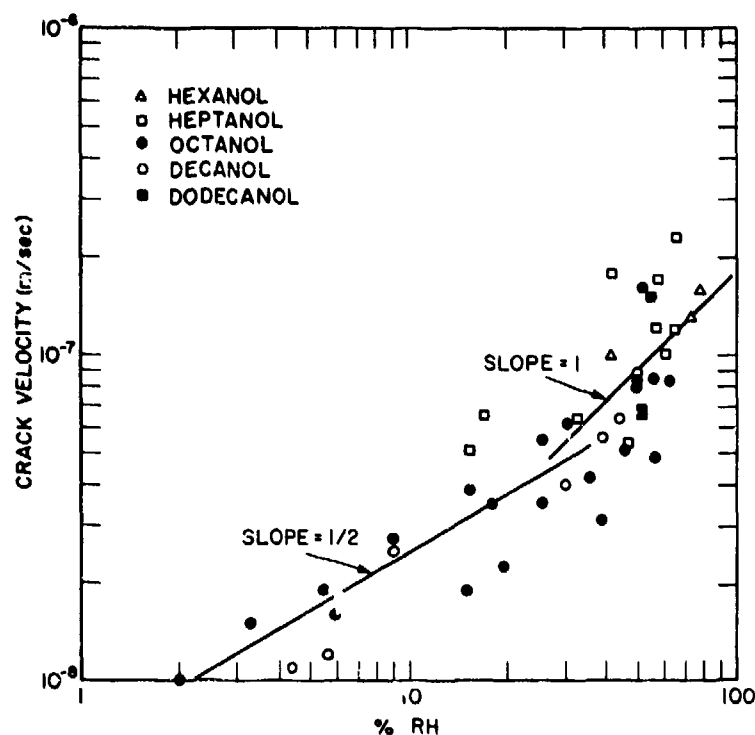


Fig. 4a -- Crack velocity in soda-lime-silica glass as a function of relative humidity in alcohols in each of the regions of the V -vs- K plot (Fig. 3) Region 1: $K = 4.5 \times 10^6 \text{ Nm}^{-3/2}$

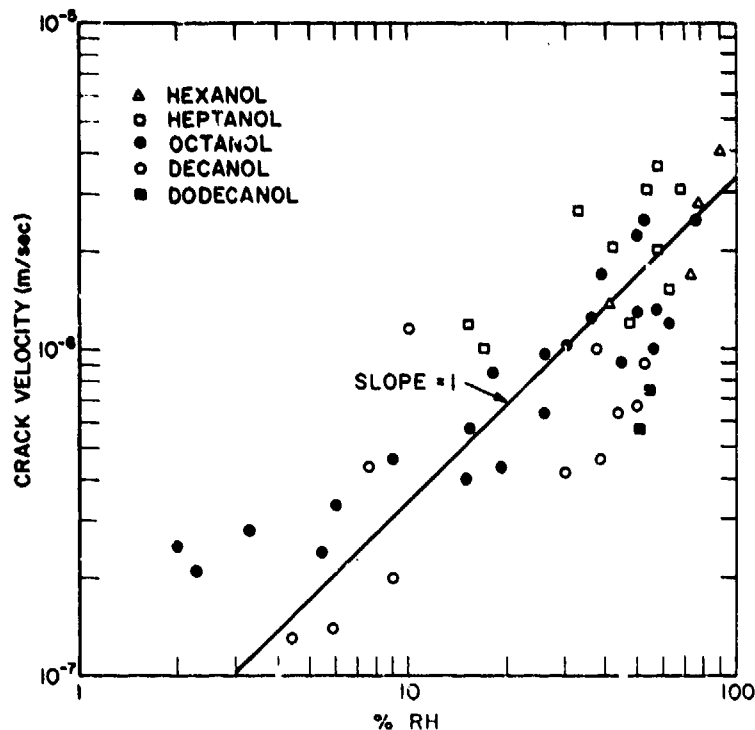


Fig. 4b — Crack velocity in soda-lime-silica glass as a function of relative humidity in alcohols in each of the regions of the V -vs- K plot (Fig. 3) Region 2: $K = 6.2 \times 10^5 \text{ Nm}^{-3/2}$

Because of the sensitivity of K to small changes in specimen geometry, K could be calculated from the load only after the test was completed and the specimen was accurately measured at a number of points. To compare the effect of humidity at the same K , a particular K was chosen to represent each region and the measured velocity was adjusted to the velocity at the chosen K using the fact that

$$\frac{V_2}{V_1} = e^{b(K_2 - K_1)}, \quad (4)$$

where b is the slope of the V -vs- K plot in the region of interest.

Although there is scatter in the data, it appears from the best-fit straight lines of slopes $1/2$ and 1 in Fig. 4a that the present data behave in a similar manner to that observed by Wiederhorn in region 1, the major difference being that the transition in slope occurs at higher relative humidities in the alcohols than in N_2 gas. Within the scatter of the data, all of the alcohols fit on the same curve, suggesting that the partial pressure of water in the alcohol is more important than its absolute quantity in solution. This may be expected, since the chemical potential of a component depends on its partial pressure in the phase.

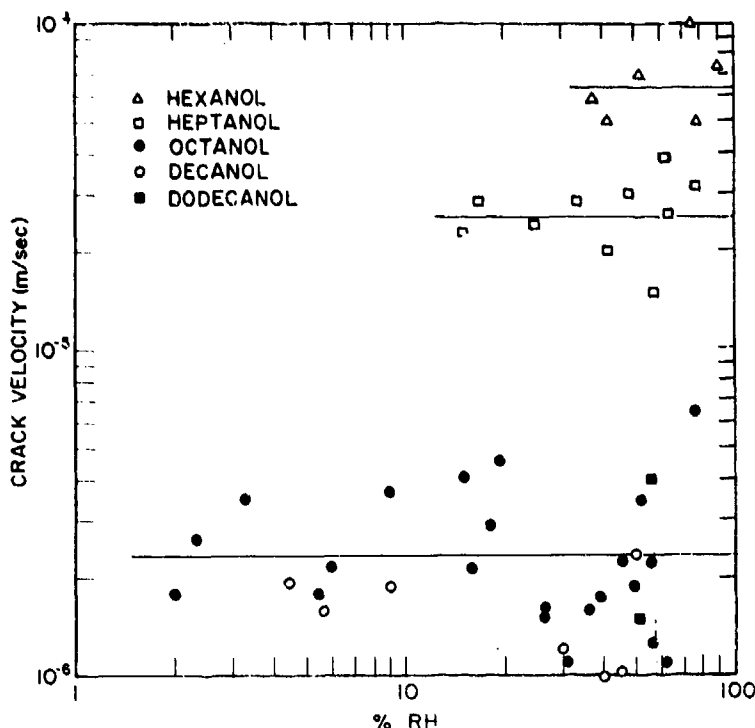


Fig. 4c — Crack velocity in soda-lime-silica glass as a function of relative humidity in alcohols in each of the regions of the V -vs- K plot (Fig. 3) Region 3: $K = 7.0 \times 10^5 \text{ Nm}^{-3/2}$

The data presented in Fig. 4b have been fit by a straight line of slope = 1 in accordance with Eq. 2. Again the chain length of the alcohol has no effect on the results.

Fig. 4c shows that crack velocity in region 3 is in fact independent of the water content of the alcohols, similar to the results observed for water in N_2 gas. In this region the chain length of the alcohol does have an effect on crack velocity, at least for alcohols having $6 < N < 8$. This same effect can be seen in the V -vs- K plot of Fig. 3.

To gain more information regarding the mechanism of crack growth in region 3, the temperature dependence of crack propagation rates was measured in the alcohols. Crack velocities are shown in Fig. 5 as a function of K for three temperatures in four alcohols.

There are a number of ways of analyzing the raw data, some of which are based on the assumed form of the mechanism governing the crack-growth process. The particular method one chooses can lead to conflicting conclusions regarding this mechanism. For

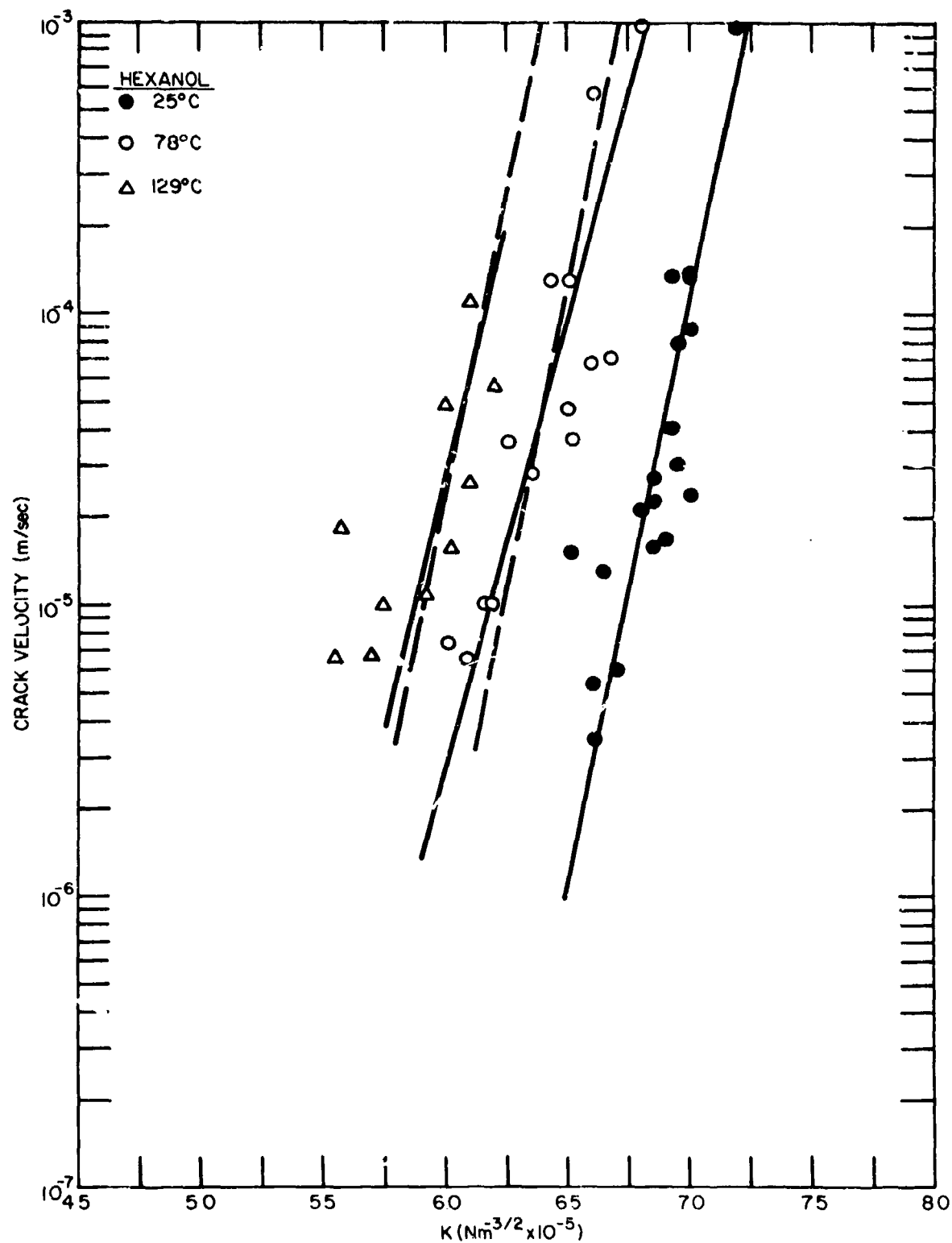


Fig. 5a — Crack propagation in hexanol as a function of temperature. Solid lines are best-fit straight lines; dashed lines were drawn assuming no change in slope with temperature.

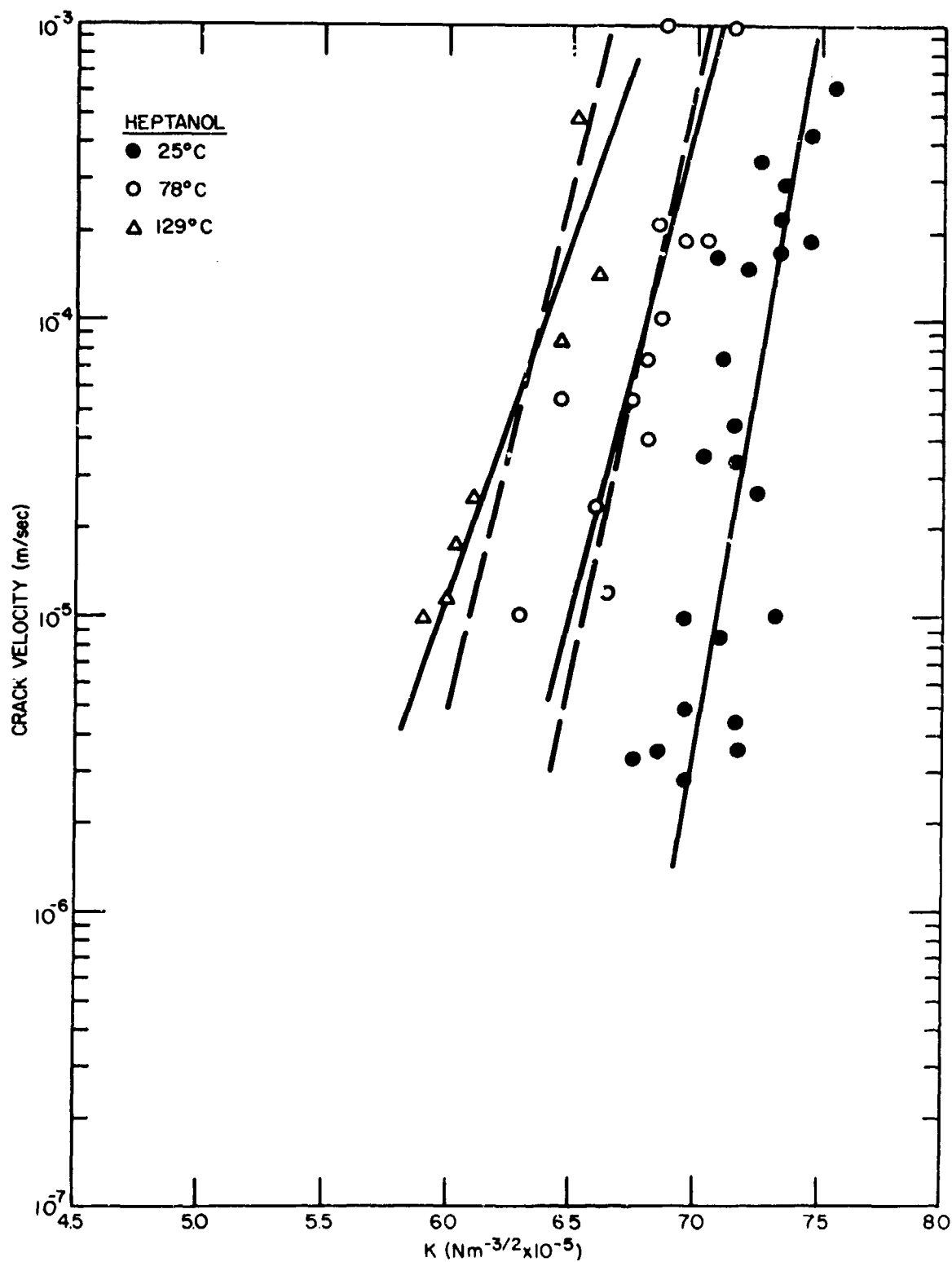


Fig. 5b — Crack propagation in heptanol as a function of temperature. Solid lines are best-fit straight lines; dashed lines were drawn assuming no change in slope with temperature.

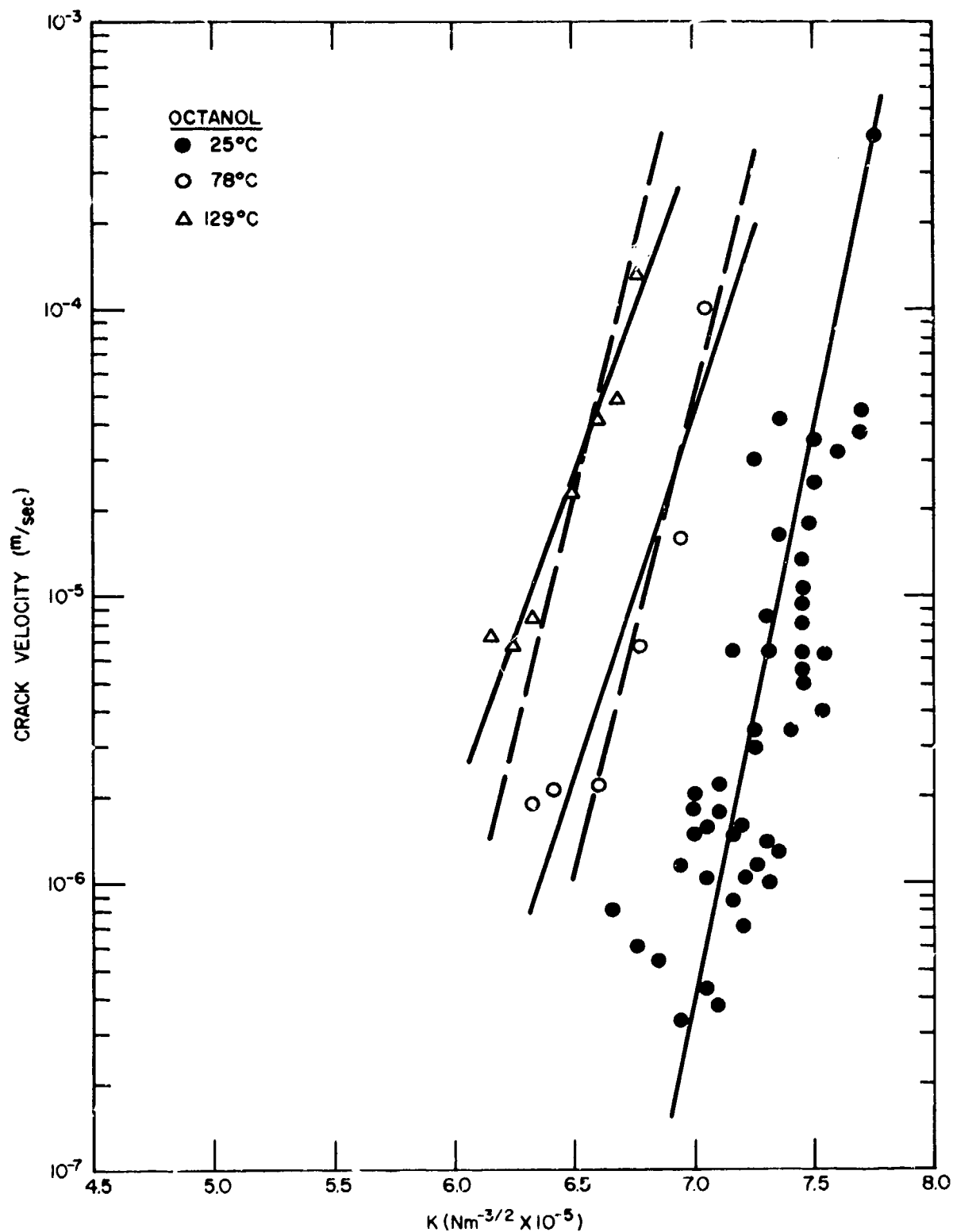


Fig. 5c — Crack propagation in octanol as a function of temperature. Solid lines are best-fit straight lines; dashed lines were drawn assuming no change in slope with temperature.

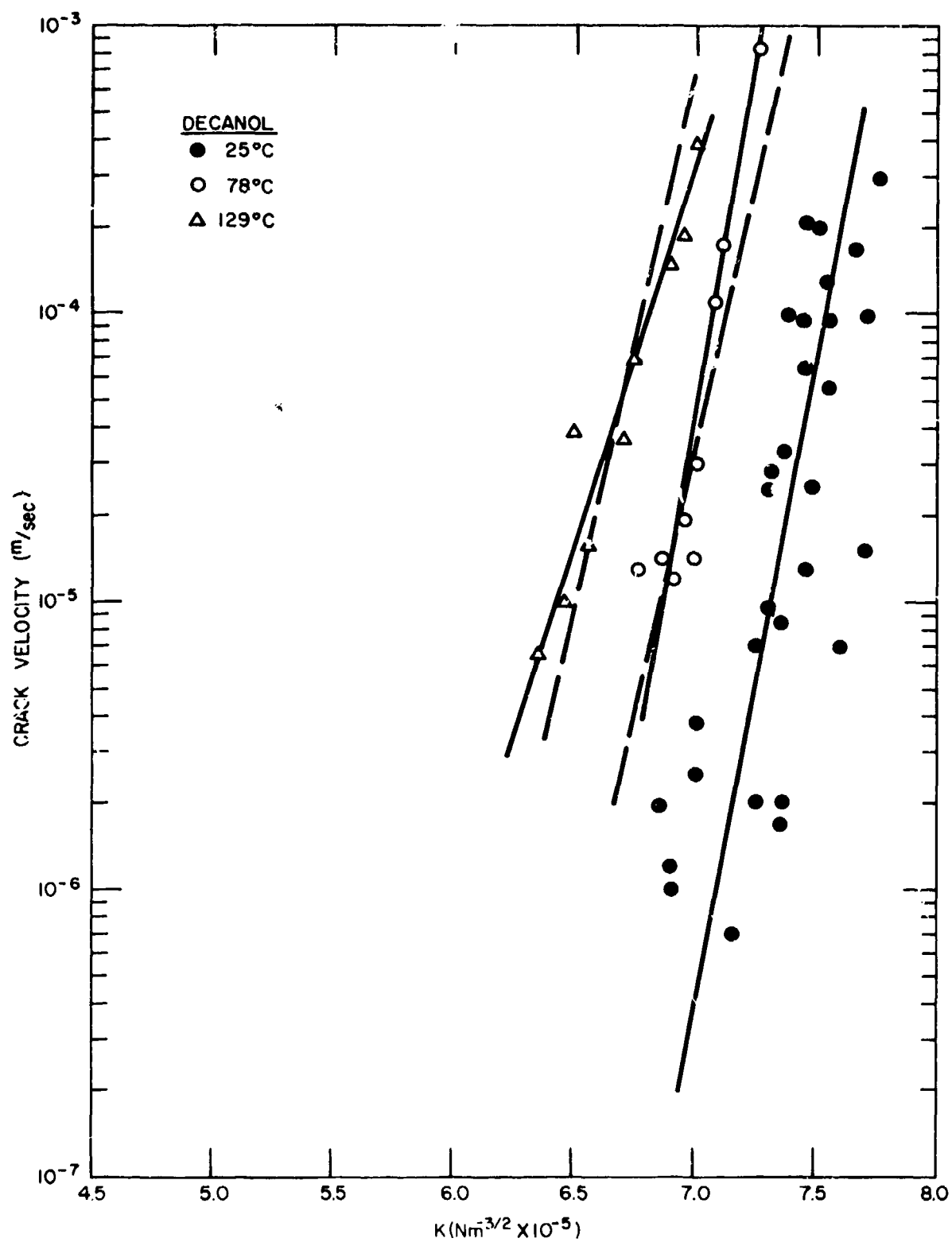


Fig. 5d — Crack propagation in decanol as a function of temperature. Solid lines are best-fit straight lines; dashed lines were drawn assuming no change in slope with temperature.

instance, for a stress-corrosion mechanism, activation energy should be a function of K . The temperature dependence of crack propagation in glass in vacuum [8] has been analyzed assuming such a mechanism using an expression of the form

$$V = V_0 e^{(-E^* + bK)/RT} \quad (5)$$

or

$$\ln V = -\frac{E^*}{RT} + \frac{bK}{RT} + \ln V_0, \quad (6)$$

where V_0 and b are empirical constants and E^* is the activation energy for crack growth in the absence of stress.

Wiederhorn [8] combined all his data for all temperatures and fit these data for each glass to such an expression; in several cases there was considerable variance between the measured points and the fitted curves. Activation energies calculated from these curves ranged from 65 to 144 kcal/mole. Values this large make it difficult to relate fracture to a simple mechanism. For this reason and because it was known that the presence of water had no effect on crack propagation in region 3, this type of analysis was not used in the present study.

It is also possible to calculate E^* by treating data for each temperature independently. The data for each alcohol and temperature were fit in Fig. 5 with a best-fit straight line (solid curves), minimizing the error in K . From Eq. 6 it is seen that at the point $K = 0$ one can obtain a value for E^* from the slope of a plot of $\ln V$ versus $1/T$. Activation energies in the alcohols obtained in this way ranged from about 40 to 80 kcal/mole and varied randomly with the chain length of the alcohol. One reason for the large variation in E^* is that the $K = 0$ intercept is extremely sensitive to small changes in the slope of the K -vs- V curve. In any case these values of E^* are also unsatisfying from the point of view of understanding the crack-growth mechanism.

As was pointed out, Eq. 5 was derived on the basis that crack growth occurs by a stress-corrosion mechanism. Since crack growth in region 3 is water independent, it seems valid to assume that stress corrosion is not a significant factor, so that the activation energy of the controlling mechanism is not stress dependent. This assumption suggests that crack velocity can be expressed as a function of K and T in the following way

$$V = V_0 e^{-E^*/RT} e^{bK} \quad (7)$$

In this case the slopes of the K -vs- V curves should be temperature independent. Such temperature-independent slopes are shown as the dashed lines in Fig. 5. A chi-squared analysis used to compare these curves with the data indicate that the points can be described by these curves to within a 99+% confidence level. E^* can now be calculated from plots of $\ln V$ versus $1/T$ at any given K as shown in Fig. 6. This analysis shows that there is no apparent effect of the alcohol on the temperature dependence of crack propagation. An activation energy for crack growth (E^*) in the alcohols of 17 to 18 kcal/mole was calculated from the slopes of the curves. This activation-energy range approximates that of Na^+ ion diffusion in similar glasses [9] and suggests therefore that

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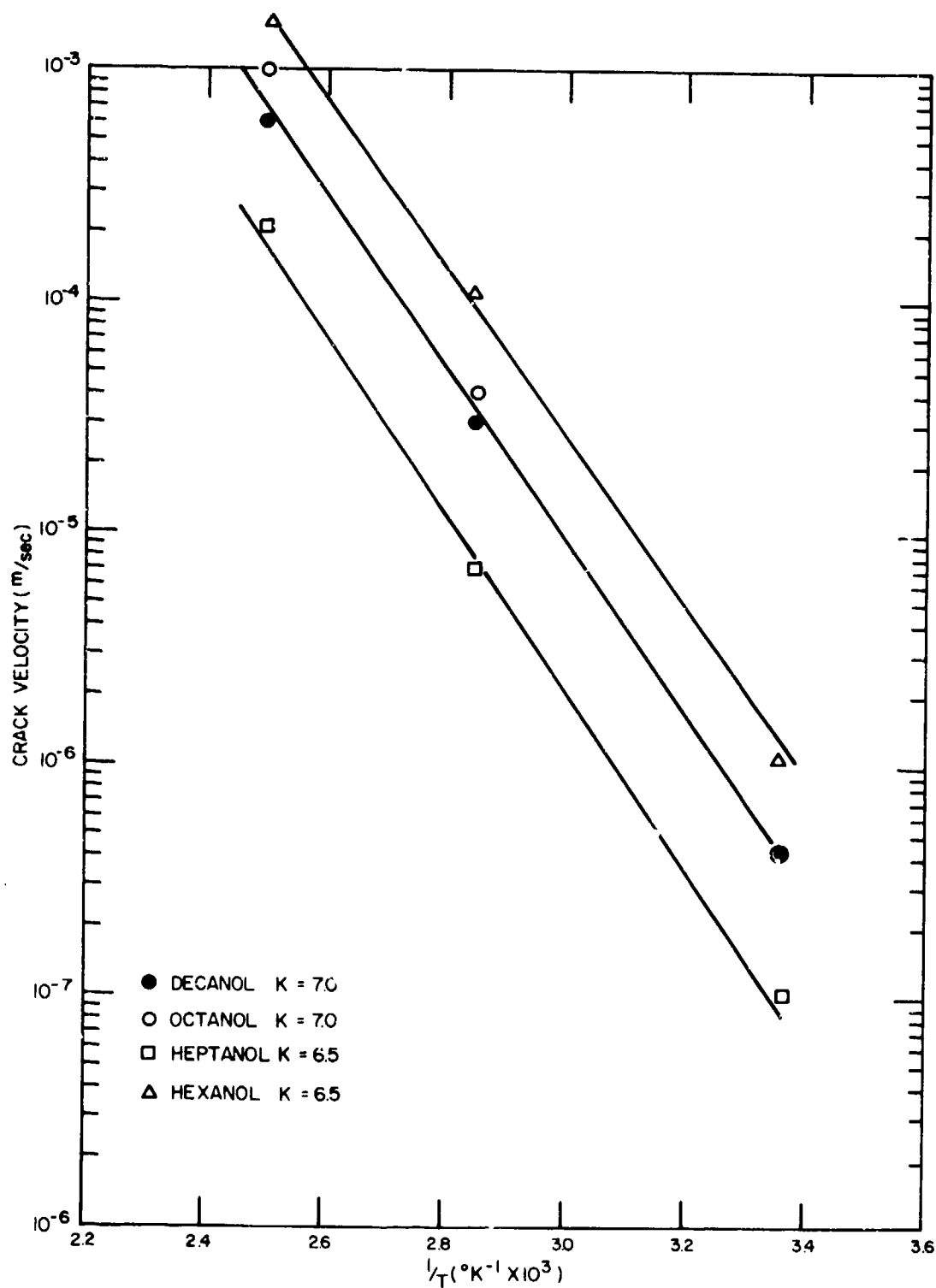


Fig. 6 — Crack velocity as a function of temperature for four alcohols

crack propagation in this regime is controlled by the rate of diffusion of ions to the crack tip. Based on the work of both Charles [10] and Weber and Goldstein [11] neither hydrostatic pressure nor tensile stresses produce large changes in the activation energy for sodium diffusion in a soda-lime-silica glass of similar composition. Their values for the activation energy for electrical conductivity range from 18 to 21 kcal/mole for glasses in various states of anneal as well as under hydrostatic pressure, or for ionic motion in a flexurally stressed glass bar. The results of Weber and Goldstein [11] suggest that alkali ions probably migrate toward the highly stressed region at the tip of a crack, weakening the bonding there due to the formation of nonbridging oxygen ions and therefore allowing the crack to propagate into the weakened region. The rate at which the crack can grow is determined by the diffusion rate of alkali ions to the crack tip. Such a mechanism of stress-induced ion migration to the crack tip, which has also been proposed by others [12] to explain crack propagation in this region, suggests that the external environment may affect diffusion processes near the free surface of a solid, as theorized by Westwood et. al. [1-3]. The effect of these environments become evident only where the more deleterious effect of moisture is not present.

The preceding mechanism suggests that crack velocities in glasses having large concentrations of alkali ions should be significantly higher for a given K than those in low-alkali glasses. The results of crack velocity experiments in both water and octanol of about 30% RH for a number of different glasses (Fig. 7) indicate that alkali ions (primarily Na^+) are not the prime factor in determining crack propagation behavior. It is apparent that significant variations in Na^+ ion concentration within the ternary soda-lime-silica system has little influence on crack propagation, whereas cracks in a $3\text{BaO} \cdot 5\text{SiO}_2$ glass containing 0.1 wt-% Na^+ propagate at a much higher velocity at any given stress intensity factor K . The fact that fused silica containing only parts per million of Na^+ and soda-lime-silica behave so similarly (Fig. 7b) also suggests that alkali content in itself is not the primary factor determining crack propagation resistance. This apparent conflict of the activation energy and compositional dependence results may be resolvable with further experimentation. The variations in E^* with analysis technique suggests that this type of study is not adequate to establish a crack-growth mechanism.

The effect of the chain length in the alkane series on crack propagation in commercial soda-lime-silica glass is shown in Fig. 8. In alkanes having six carbon atoms or greater, three regions are observed similar to those in the alcohols. In pentane ($N = 5$) however no regions 2 or 3 were obtained. Data were taken in 50-50 mixtures of pentane and hexane in the hope of more accurately determining the point at which the transition from single mode to tri-modal curves occurred. It was found however that points from some specimens fell on the curve for pentane, and points from others fell on the curve for the higher-chain-length alkanes. Measurements of relative humidity in pentane showed it to be less saturated than most of the higher chain alkanes. No explanation can be given for the difference in behavior between it and the rest of the alkane series, in which crack growth is apparently controlled by the same mechanism of stress corrosion and diffusion as in the alcohols. Region 1 data for all of the alkanes fit on the same curve. Although there is some scatter, the stress intensity at which region 2 behavior begins appears to decrease monotonically with increasing chain length. Unlike the alcohols however no effect of alkane chain length can be seen in the region 3 data.

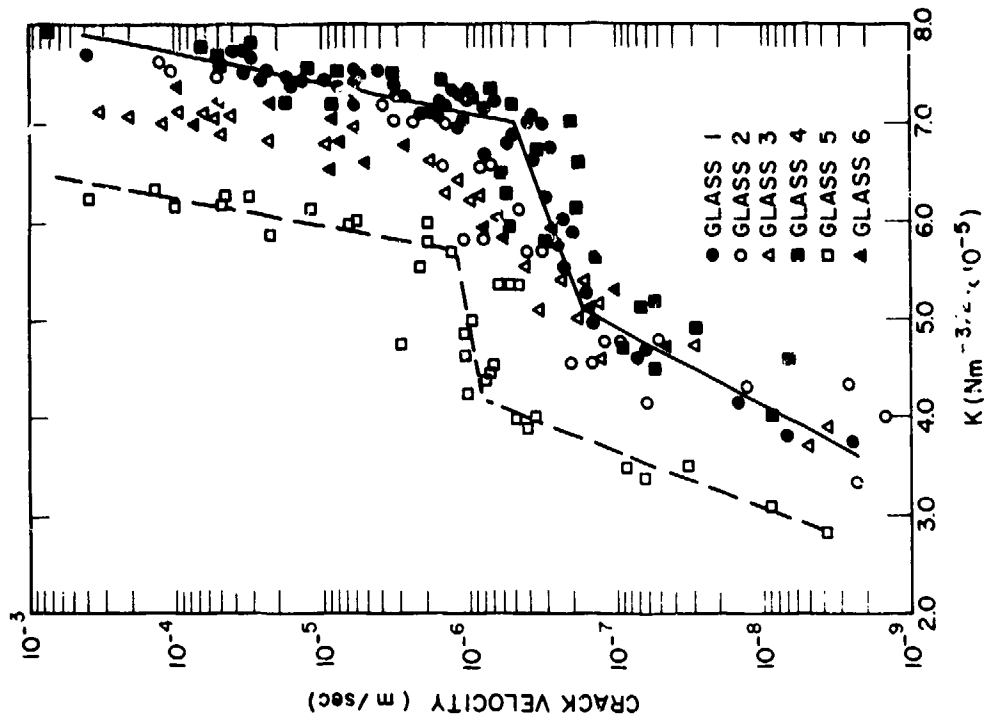


Fig. 7a — Effect of glass composition on crack propagation behavior in water

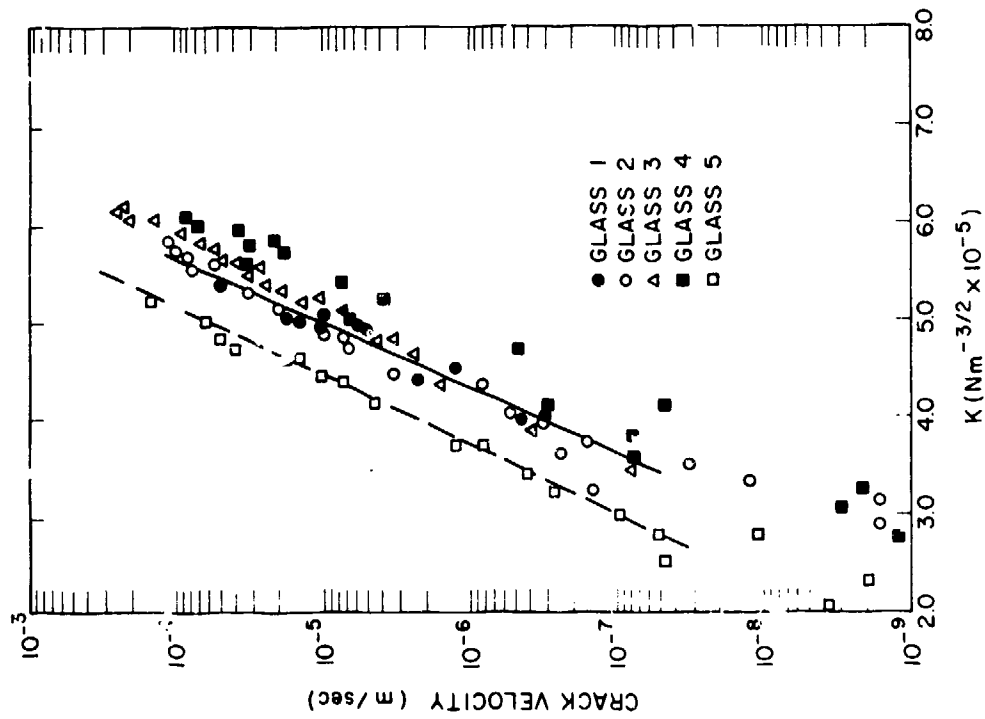


Fig. 7b — Effect of glass composition on crack propagation behavior in octanol

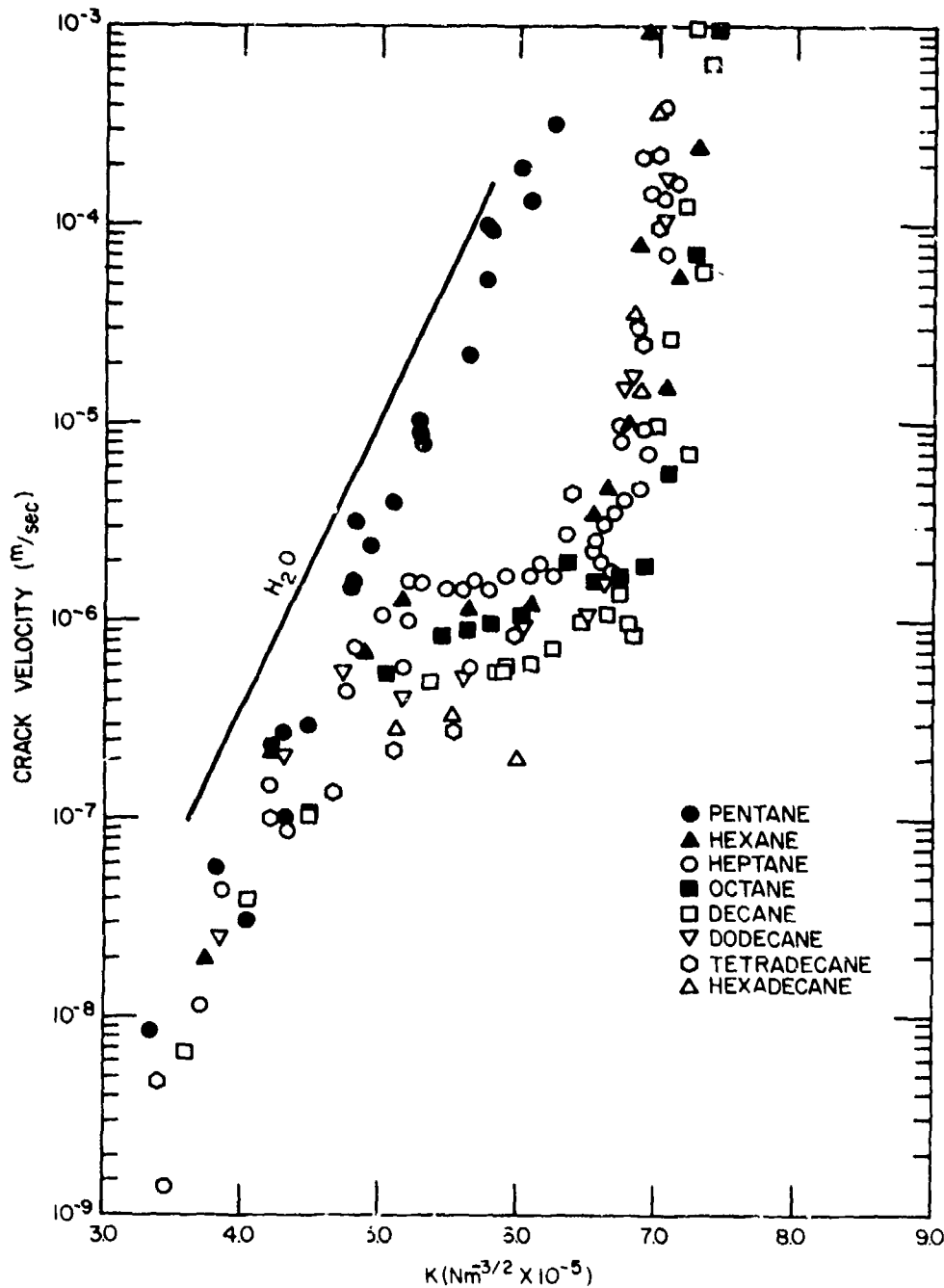


Fig. 8 — Crack velocity as a function of K for commercial soda-lime-silica glass tested in straight-chain alkanes

DISCUSSION

Westwood and coworkers [1-3] showed that drilling rates in a soda-lime-silica glass using a diamond-bit drill on specimens immersed in straight chain alcohols of various chain lengths reached a maximum in heptanol ($N = 7$). This maximum rate was over 20 times that in water. It was also found that the hardness of this glass as measured by a pendulum sclerometer was also maximized at this same chain length, although the increase was not as dramatic as the increase in the drilling rate. Similar kinds of effects were observed when straight chain alkanes were substituted for the alcohols, although the effects were not as large in magnitude.

Crack propagation is at least one of the mechanisms which influence the drilling rate in glass using a diamond bit, although its importance in determining hardness is questionable. The lack of maxima or minima in the V -vs- K plots obtained in this study demonstrates that other mechanisms must also be involved in the drilling rate and hardness phenomena. Over most of the V -vs- K range, crack velocities depended on the partial pressure of water in the alcohol but were independent of chain length. Velocities in the highest K region were independent of water content but increased monotonically with chain length at a given K . This latter effect indicates that although the mechanism of crack growth is different than the water-activated stress-corrosion mechanism at lower stress intensities, it is still environmentally dependent. Independent results [13] of crack propagation experiments performed using conventional double-cantilever or double-torsion type tests have corroborated the crack propagation data obtained in this study.

Westwood and Huntington [3] reported results using a different crack-propagation technique which showed that the energy needed to propagate a crack reached a maximum in heptanol. From their fracture energy Φ_B of glass tested in water, and the data for water presented in Figs. 3 and 4a of this study, where $\Phi_B = K^2/2E$, one can estimate that their crack velocities were in the range of 2×10^{-7} to 4×10^{-7} m/s. In this range crack velocity is not very sensitive to change in K . On the other hand it is evident that the K required to drive the crack in this velocity region is quite sensitive to changes in the partial pressure (RH) of water in the alcohols. In fact, crack growth varies from reaction-rate-controlled growth (region 1) to diffusion-controlled growth (region 2), depending on RH.

From the preceding information and the measured relative humidity of the alcohols after exposure to the atmosphere (Fig. 2), Φ_B can be calculated to vary from approximately 1.3×10^3 to 2.3×10^3 ergs/cm², depending on relative humidity, compared with Westwood's values, which range from 1.1×10^3 to 2.4×10^3 ergs/cm². This leads to the conclusion that the differences in Φ_B observed by Westwood and Huntington are probably due to changes in the water content of their alcohols. Their conclusion that Φ_B is maximized in heptanol is therefore highly questionable. It should be noted that the results of this study show that the partial pressure rather than the total quantity of water is important.

Westwood et al. [2] have proposed that their measured property variations are due to small changes in sodium or hydroxyl ion concentration at the surface of the glass, which occur because of variations in surface potential produced by the liquids. The

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relatively small effect which glass composition within the soda-lime-silica system has on crack growth and its similarity in behavior to that of fused silica which contains only a few parts per million of alkali (Fig. 7b) raises a question whether the small changes in composition produced by surface charges could cause such large changes in hardness and drilling rates. The much higher crack velocities in the $3\text{BaO} \cdot 5\text{SiO}_2$ glass compared to those in the soda-lime-silica glasses suggests that alkali content of itself may be only a minor factor in determining stress-corrosion rates.

It has been shown in this study that changes in crack-propagation behavior alone cannot explain the observed maximum in drilling rate in glasses. The possibility that the maximum may be due to an increasing resistance to crack propagation with alcohol chain length, coupled with a decreasing coefficient of friction [14], which is also an important parameter in drilling, should be the subject of future research.

SUMMARY

Crack velocities were measured as a function of stress intensity factor K for glasses immersed in straight chain alcohols ($6 \leq N \leq 12$) and alkanes ($5 \leq N \leq 16$). Three regions of behavior corresponding to three ranges of K were observed in the alcohols. In regions 1 and 2 crack propagation rates were a function of the partial pressure of water in the alcohol and were governed by the stress-corrosion rate at the crack tip and the rate of diffusion of water to the tip respectively. Crack propagation behavior in these regions fit a model proposed by Wiederhorn for crack growth in moist gas and extended in this work to include water dissolved in another liquid. No dependence of crack propagation on alcohol chain length was observed in regions 1 and 2. In the highest K region (region 3) crack velocities were independent of the partial pressure of water, but a monotonic increase in crack velocity at a given K was observed as the chain length of the alcohol decreased. It was therefore concluded that the maximum in drilling rate in heptanol observed by Westwood and coworkers cannot solely be due to the effect of the liquid on crack propagation. Based on the assumption that E^* is independent of K in region 3, an activation energy of 17 to 18 kcal/mole was determined for crack growth in this region, which was independent of the chain length of the alcohol. This activation energy suggested that the growth is controlled by stress-enhanced Na^+ diffusion in the glass, with the diffusion rate influenced by the external environment. However, the insensitivity of crack propagation to changes in Na^+ concentration from ppm to 25% implies that mechanisms may be more complicated than simple diffusion.

All of the alkanes except for pentane yielded results similar to the alcohols. No reason for the behavior of pentane could be given.

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